

## Transition Metal Catalysis in Porphyrin Modifications

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*A mini-review covers the results obtained by the authors in porphyrin modifications using Pd and Cu-catalyzed amination of halogenophenyl substituted porphyrins. Amination using primary and secondary linear and cyclic amines and diamines, formation of polymacrocyclic conjugates of aza- and diazacrown ethers and diazacrown ether-based cryptands with porphyrins are addressed. Synthesis of diporphyrin and triporphyrin systems via Pd-catalyzed amination and Cu-catalyzed “click” reactions are discussed.*

**Keywords:** Porphyrins, macrocycles, catalysis, amination.

## Катализ переходными металлами в модификациях порфиринов

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*Данный мини-обзор посвящен результатам, полученным авторами при модификации порфиринов с использованием Pd- и Cu-катализируемого аминирования галогенфенилзамещенных порфиринов. Рассматриваются аминирование с использованием первичных и вторичных линейных и циклических аминов и диаминов, образование полимакроциклических конъюгатов порфиринов с аза- и диазакраун-эфиром и криптандами на основе диазакраун-эфиров. Обсуждается синтез ди- и трипорфириновых систем с использованием Pd-катализируемого аминирования и Cu-катализируемых «клик-реакций».*

**Ключевые слова:** Порфирины, макроциклы, катализ, аминирование.

### Introduction

Modification of porphyrins using catalytic approaches is a modern and versatile tool for creating numerous derivatives of these unsaturated tetraazamacrocycles decorated with different functionalities, for the synthesis of sophisticated polymacrocyclic architectures comprising several porphyrin units (dyads and triads) or smart conjugates of porphyrins with other macrocyclic moieties. Hundreds of works have been already published dealing with various aspects of this topic, and corresponding information has been collected and organized in a comprehensive review in 2012.<sup>[1]</sup> A short outline of the catalytic transformations of porphyrins

should start from the application of the reactions of C-C bond formation. Suzuki coupling is well documented since 1994 when this reaction was first applied by Zhou for the exocyclic transformation of the porphyrin core,<sup>[2]</sup> porphyrin bearing halogen atoms<sup>[3]</sup> and borylated porphyrins<sup>[4]</sup> both find their applications in constructing new carbon-carbon bonds. The same is true for Sonogashira reaction which was first applied for the porphyrin modifications also in 1994,<sup>[5]</sup> and halogen-substituted porphyrins<sup>[6]</sup> as well as porphyrins with acetylene moieties<sup>[7]</sup> participate in the coupling. Heck and so-called “click” reactions were also among those which were successfully applied to the creation of new C-C bonds in porphyrins, the first one applied to porphyrin modifications

dates back to 1998<sup>[8]</sup> while the second one began to be widely employed a decade later<sup>[9]</sup> and is especially useful for the conjugation of porphyrins with various pharmacophores, sugars, oligonucleotides, fullerene, and moieties used for immobilization.

Catalytic formation of C-N bonds according to Buchwald-Hartwig protocol, which is of especial value for our own research, till last time has been widely used for the introduction of quite simple substituents. In 2003 Chen and Zhang reported the first successful amination of mono- and di-*meso*-halogeno substituted porphyrins and their Zn complexes with primary aliphatic and aromatic amines.<sup>[10]</sup> In the same 2003 Suda studied Pd-catalyzed amination reactions of *meso*-bromosubstituted porphyrins using Pd(0) and Pd(II) catalysts with a variety of phosphine ligands.<sup>[11]</sup> Lier claimed first catalytic amination of Zn complexes of mono- and di- $\beta$ -halogenoporphyrins with aliphatic and aromatic amines in 2001.<sup>[12]</sup> Zhang was the first who employed Pd(OAc)<sub>2</sub> for di- and tetraamination of bis- and tetrakis(4-bromophenyl) substituted porphyrins.<sup>[13]</sup> The year of 2003 was extremely fruitful for the pioneer works in the field of C-N bond formation in porphyrin series: Suda reported amidation of Zn and Ni *meso*-bromoporphyrin complexes with primary and secondary amides in the presence of Pd(OAc)<sub>2</sub>/BINAP.<sup>[14]</sup> Zhang modified this method applying Pd(OAc)<sub>2</sub>/Xantphos system which allowed diamidation of di-*meso*-bromoporphyrins in high yields.<sup>[15]</sup> In 2001 amidation of  $\beta$ -bromoporphyrins using cyclic amides in the presence of Pd(dppf)Cl<sub>2</sub>/dppf was reported by Lier,<sup>[12]</sup> and in 2007 Zhang proposed an universal approach for the amidation of mono- and dibromoporphyrins and their metal complexes using Pd<sub>2</sub>(dba)<sub>3</sub> or Pd(OAc)<sub>2</sub> with Xantphos ligand.<sup>[16]</sup>

Alkoxy- and aryloxylation reactions of mono- and di-*meso*-bromophenylporphyrins catalyzed by Pd(OAc)<sub>2</sub> or Pd<sub>2</sub>(dba)<sub>3</sub> with DPEphos or Xantphos were described in 2003 by same Zhang.<sup>[17]</sup> In 2007 he was also the first who reported on successful synthesis of  $\beta$ -substituted alkoxy- and aryloxyporphyrins using Pd<sub>2</sub>(dba)<sub>3</sub>/DPEphos catalytic system and made chiral diporphyrin conjugates using catalytic C-O bond formation.<sup>[18]</sup> His group pioneered in the catalytic sulfanylation of mono- and di-*meso*-bromoporphyrins employing the same catalytic system.<sup>[19]</sup> Later on the catalytic synthesis of the first porphyrin-containing phosphineoxide was published,<sup>[20]</sup> followed by the work of Guilard and Tsvadze in which di- and tetraphosphonylated porphyrins were synthesized using Pd(OAc)<sub>2</sub>/PPH<sub>3</sub> catalytic system.<sup>[21]</sup>

As borylated porphyrins were found to be very useful building blocks for the synthesis of covalent porphyrin dimers and oligomers, their synthesis attracted much attention. Pinacol borane and bis(pinacol) borane are the most widely used reagents for this purpose. Therien<sup>[22]</sup> proposed an earlier described Masuda protocol<sup>[23]</sup> to be employed in the synthesis of mono- and di-*meso*-substituted porphyrins from pinacol borane and corresponding zinc (di)bromoporphyrinates using Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, this approach was further developed by Zhang and Suslik.<sup>[24]</sup> Pd(dppf)Cl<sub>2</sub> was helpful for the borylation of 2-bromosubstituted porphyrin,<sup>[25]</sup> and the methodology was spread for the synthesis of tetra-*meso*-borylated compounds.<sup>[26]</sup>

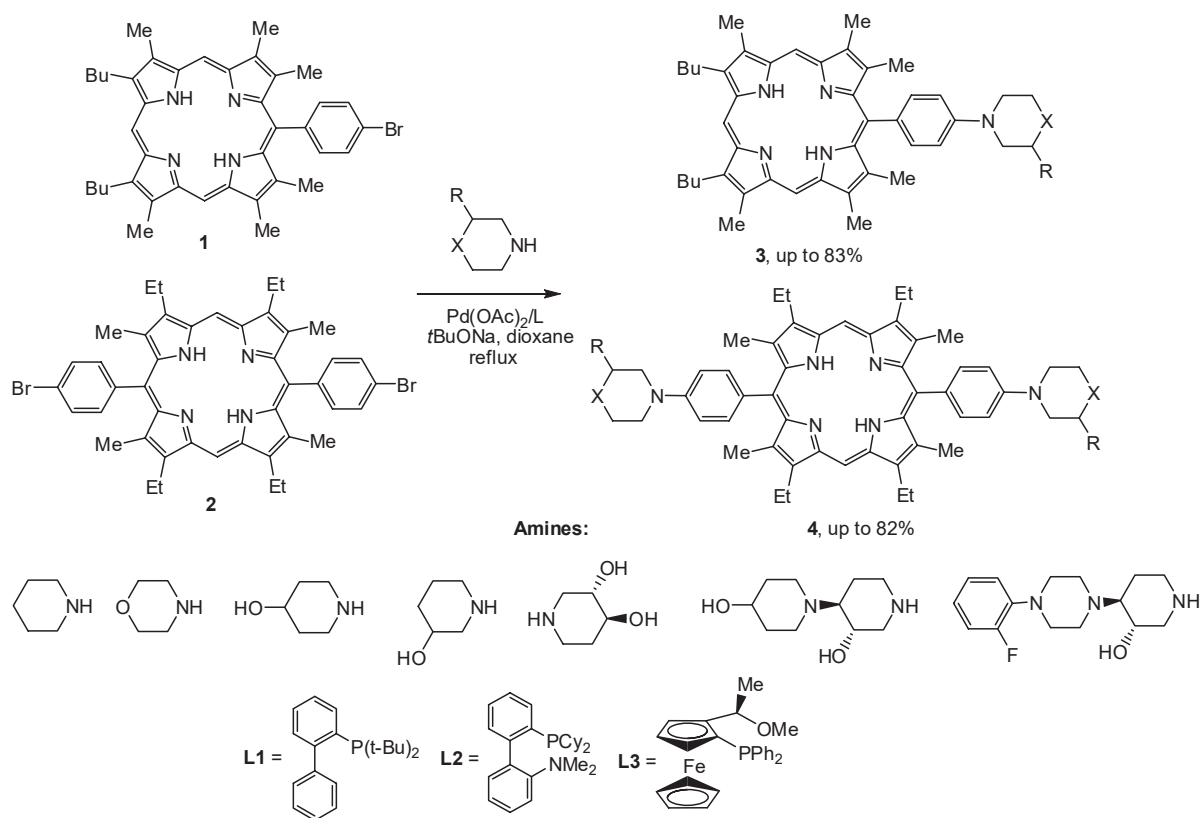
An important aspect of the catalytic transformations of porphyrins is the synthesis of polyporphyrin species. *meso-meso*-Conjugated porphyrin dimer<sup>[27]</sup> and trimer<sup>[28]</sup> without a linker were synthesized using Suzuki coupling, the same approach was used for the synthesis of dimers with face-to-face organized porphyrin units attached to aromatic linkers,<sup>[29]</sup> as well as for a linear trimer.<sup>[30]</sup> Stille coupling was used for the synthesis of various porphyrin dimers,<sup>[31,32]</sup> especially for the derivatives with long polyene systems.<sup>[33]</sup> Heck and Sonogashira reactions are also widely employed for the synthesis of bisporphyrin compounds with different linkers including acetylenic fragments,<sup>[34]</sup> the latter approach was helpful in the synthesis of porphyrin trimers as well.<sup>[35]</sup> Catalytic amination and alkoxylation reactions were successfully applied to the synthesis of porphyrin dimers and trimers.<sup>[36]</sup> Cu(I)-catalyzed 1,3-dipolar cycloaddition reactions can be also used for the synthesis of porphyrin dyads with 1,2,3-triazole linkers.<sup>[37]</sup> Above-mentioned catalytic reactions were widely used also for creating bis- and trisporphyrin systems with  $\beta$ - $\beta$  and  $\beta$ -*meso* conjugation, and *para*-phenylene linkers were the most widely used in all these processes including metathesis reactions.<sup>[38]</sup>

A special interest is attracted by the catalytic reactions leading to macropolycyclic compounds comprising porphyrin structural units. For example, Heck reaction was used for the synthesis of the macrotricycle in which two crown ethers are fused with the central porphyrin moiety.<sup>[39]</sup> Suzuki coupling allowed the synthesis of pentamacrocycle with three porphyrin units,<sup>[40]</sup> while the metathesis reaction, which used the template effect of tetra-*meso*-pyridylporphyrin, allowed the synthesis of a huge tetraporphyrin macrocycle.<sup>[41]</sup> All these data clearly demonstrate efficiency and versatility of the catalytic approaches in the porphyrin transformations.

## Catalytic Amination of *meso*-(Bromophenyl) Substituted Porphyrins

Our own contribution to the field of catalytic transformation of porphyrins deals mainly with the Pd-catalyzed amination reactions and the first works published in 2008<sup>[42,43]</sup> considered the reactions of  $\beta$ -octaalkylated mono- and di-*meso*-(4-bromophenyl)porphyrins **1** and **2** with a variety of cyclic amines, especially hydroxypiperidines, which are the simplest analogues of polyhydroxylated piperidine alkaloids used as HIV replication inhibitors. The reactions employed Pd(OAc)<sub>2</sub> as the source of palladium, several electron-donor phosphines ligands were checked, and among them biphenyl-based ligands **L1** and **L2** and ferrocene-derived ligand **L3** were found to be most efficient providing yields of monoaminated derivatives **3** up to 83 % and yields of diaminated derivatives **4** up to 82 % (Scheme 1). In the case of di(bromophenyl)porphyrin **2** the formation of side products of monoamination with the reduction of C-Br bond was noted, and in the case of monobromide **1** the formation of *meso*-phenylporphyrin also due to the catalytic reduction was observed with several amines.

Our further development of the Pd-catalyzed amination of *meso*-(4-bromophenyl)porphyrin was focused on the



Scheme 1.

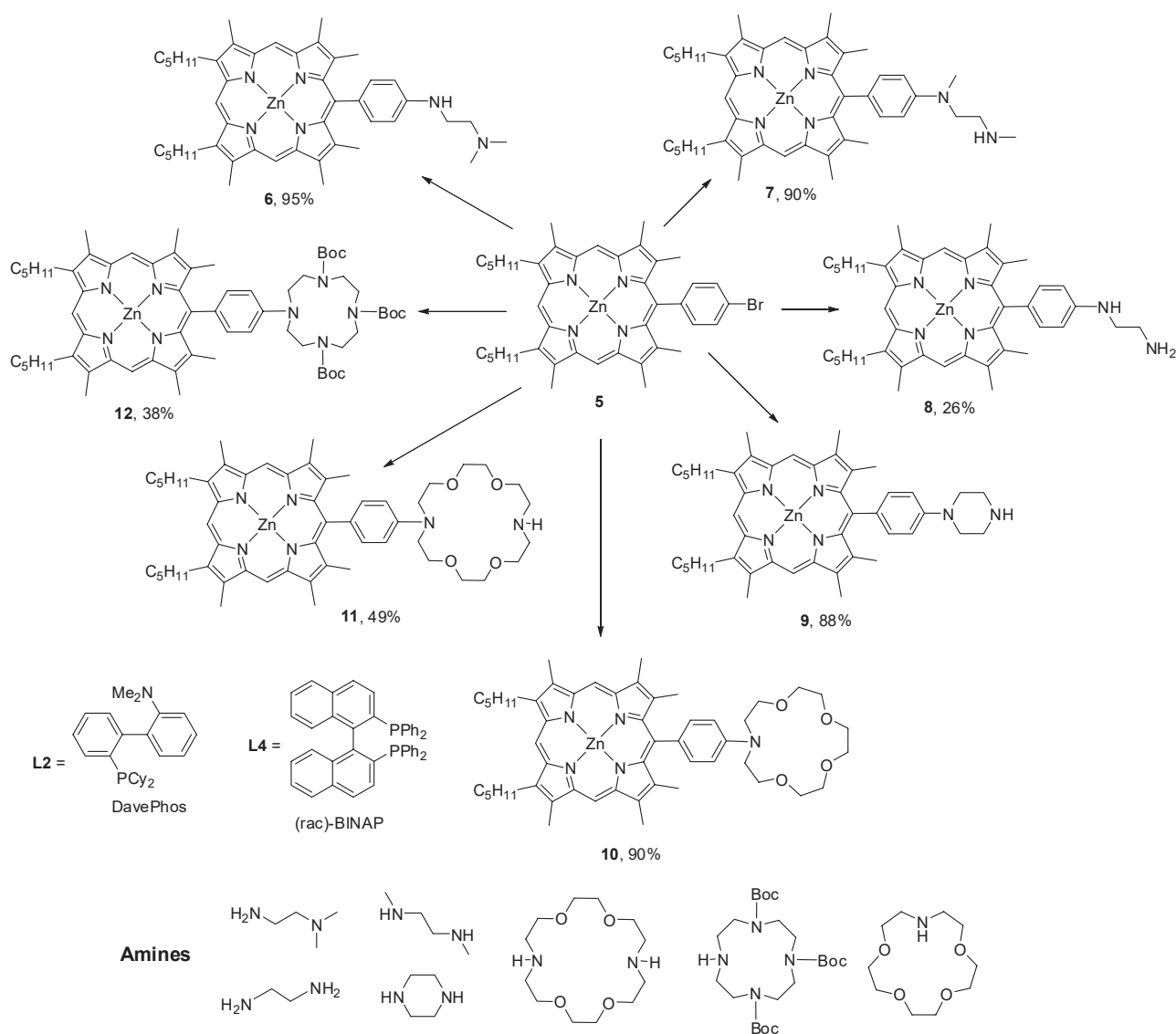
reactions of its Zn(II) complex **5** with various primary and secondary amines using Pd(dba)<sub>2</sub> as a source of palladium as it was shown to be advantageous over Pd(II) acetate in many other catalytic amination reactions. The efficiency of two most universal phosphine ligands, *i.e.* DavePhos (**L2**) and BINAP (**L4**) were compared in the reactions with ethane-1,2-diamine and its *N*-methyl derivatives, piperazine, diaza-18-crown-6 ether and *N,N,N'*-triBOCcyclen (Scheme 2).<sup>[44,45]</sup> The reactions were carried out using 1.5 equiv. of macrocyclic polyamines and 5 equiv. of other diamines to prevent *N,N'*-diarylation. As a result, the reaction with both isomers of dimethylethane-1,2-diamine, piperazine and even much more problematic 1-aza-15-crown-5 ether gave excellent yields of the amination products **6**, **7**, **9**, **10** (88-95 %) while the reaction with the simplest ethane-1,2-diamine proceeded with difficulties, possibly due to unfavorable chelation of Pd by this diamine. The reactions with diazacrown ether and triBOC cyclen afforded quite reasonable yields of the products **11** and **12** (49 and 38 %, respectively), especially comparing with our own results dealing with the Pd(0)-catalyzed arylation of these compounds using more simple aryl halides which provided 32-45 % yields of corresponding *N*-aryl derivatives.<sup>[46,47]</sup>

The next step in the application of Buchwald-Hartwig amination for porphyrins modifications was done using 5,15-di(4-bromophenyl)porphyrin **13** (Scheme 3). To promote diamination process, the reactions were carried out using 10 equiv. of diamines in the presence of Pd(dba)<sub>2</sub>/BINAP (8/16 mol%). As a result, diamino derivative **14** was obtained in 50 % yield from the unsymmetrical *N,N*-dimethylethane-1,2-diamine with a primary amino group

together with the product of monoamination and reduction of one C-Br bond (compound **15**, 32 % yield). However, the reaction with the secondary diamine piperazine was less successful and corresponding product of diamination **16** was isolated only in 19 % yield while compound **17** with one new C-N bond was obtained in a two-fold higher yield. The reaction with 1-aza-15-crown-5 ether and diaza-18-crown-6 ether were conducted using 3 equiv. of this cyclic diamines and Pd(dba)<sub>2</sub>/BINAP catalytic system providing only insignificant amount of the corresponding bis(azacrown) derivatives **18** and **20**. The application of DavePhos was helpful and it afforded good yields of the target compounds **18** and **20** (64 and 63 %, respectively), while the monoamination products **19** and **21** were also obtained in 30 and 36% yields. However, the same catalytic system did not allow the formation of bicyclic product in the reaction with 3 equiv. of triBOCcyclen, but rather gave monocyclic derivative **22** in 50% yield. Almost in all cases the formation of 5,15-diphenylporphyrin, the product of the double reduction of two C-Br bonds, was observed.

Coordination properties of the compounds **10** and **18** towards Na(I) and K(I) cations were studied using UV-vis spectroscopy.<sup>[45]</sup> It was found that coordination of these ligands with sodium cation provided complexes of **10**·Na(I) and **18**·2Na(I) compositions, while a bigger potassium cation formed complexes of 2(**10**)·K(I) and 2(**18**)·2K(I) compositions, respectively.

Tetrakis-*meso*-(4-bromophenyl)porphyrins **22** and **23** with expanded  $\pi$ -systems were introduced in the amination reactions using Pd(dba)<sub>2</sub>/L2 or Pd(dba)<sub>2</sub>/L4 catalytic systems (Scheme 4).<sup>[48]</sup> The reactions were run using 6 equiv. of



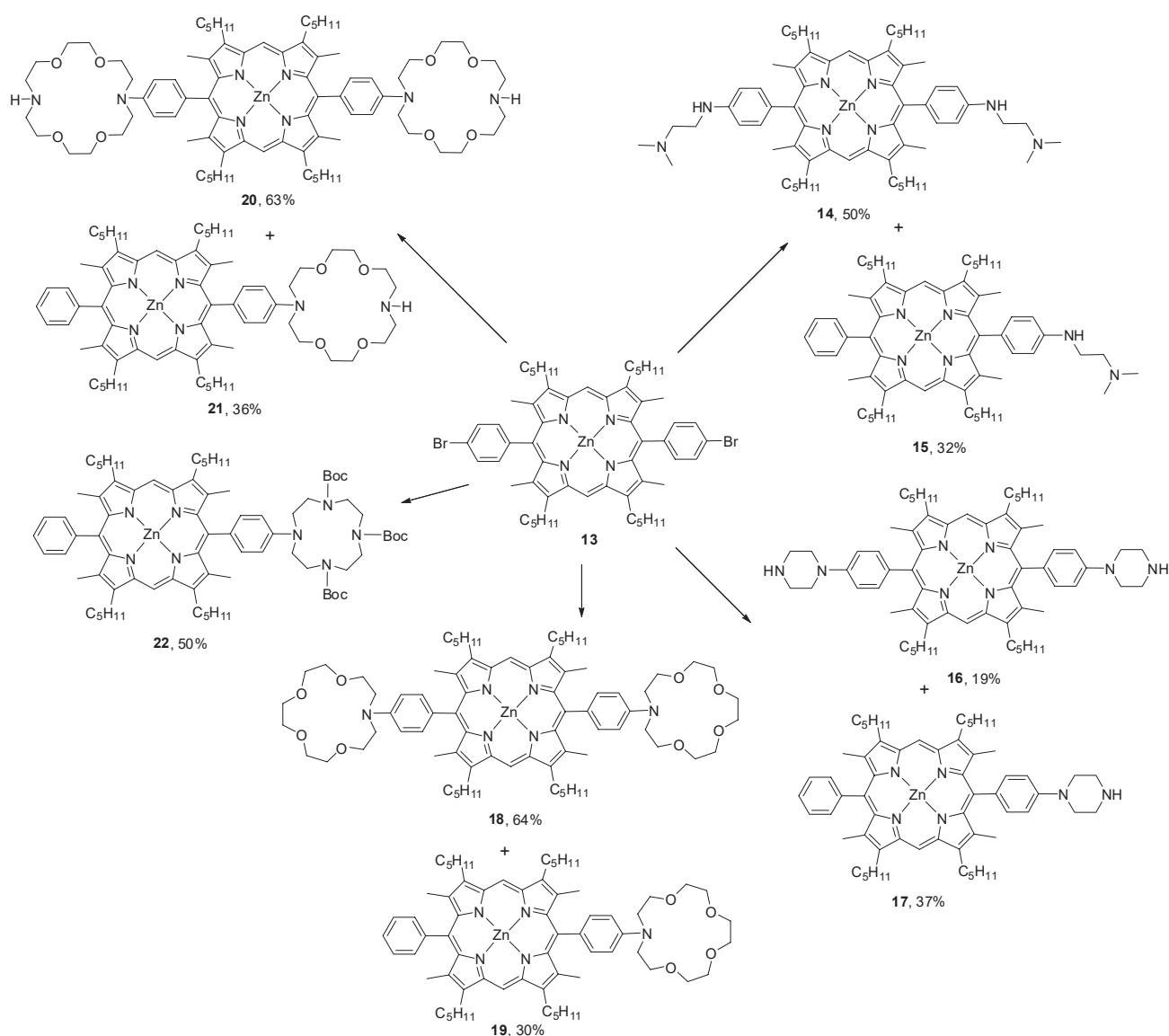
Scheme 2.

amines differing by the nature of the amino groups (primary aliphatic, primary aromatic, secondary aliphatic, dioxadiazine with two primary aliphatic amino groups). Generally, the reactions with the derivatives of tetrabenzoporphyrins provided better yields of the products of tetraamination than the derivatives of tetranaphthoporphyrins, however in the case of morpholine a higher yield in the reaction with tetranaphthoporphyrin **23** was achieved by changing BINAP for DavePhos. The reaction of tetrabenzoporphyrin **22** with 6 equiv. of 1-aza-18-crown-6 ether gave a mixture of two products: target pentamacrocycle **31** and tetramacrocycle **32** produced by the catalytic reduction of C-Br bond. This reaction could be carried out only in the presence of Pd(dba)<sub>2</sub>/L2 catalytic system.

The application of a much cheaper copper instead of expensive palladium in the catalytic reactions is a serious challenge of modern synthetic organic chemistry. We tried it in the modification of porphyrins with one and two (oxa)diamine podands. For this purpose, we compared the possibilities of Pd(0) and Cu(I)-catalyzed amination of *meso*-(halogenophenyl)porphyrins with trioxadiazine

(Scheme 5), in the experiment with palladium catalysis we used bromophenyl derivative **5** while for copper catalysis an iodophenyl substituted porphyrin **33** was applied. The yields of the corresponding trioxadiazine derivatives **34** and **36** were rather low, however, in the reaction with a simple propane-1,3-diamine the copper-catalyzed reaction was quite successful and provided 50% conversion of the starting porphyrinate **33** into the target product **35**.<sup>[49]</sup> It should be noted that only metallated porphyrins can participate in the copper-catalyzed couplings unlike in palladium-catalyzed reactions, this fact can be explained by the formation of stable complexes of free porphyrins with copper eliminating it from the catalytic cycle.

Pd(0) and Cu(I)-catalyzed diamination of di-*meso*-(bromophenyl)porphyrins **13**, **37** and **38** clearly demonstrated that palladium catalysis was advantageous over copper catalysis as the first approach allowed to synthesize porphyrin bis(diamino) derivatives **39**, **41** in reasonable yields while in the presence of copper-based catalytic systems target compounds were observed only in the reaction mixtures in insignificant amounts.



Scheme 3.

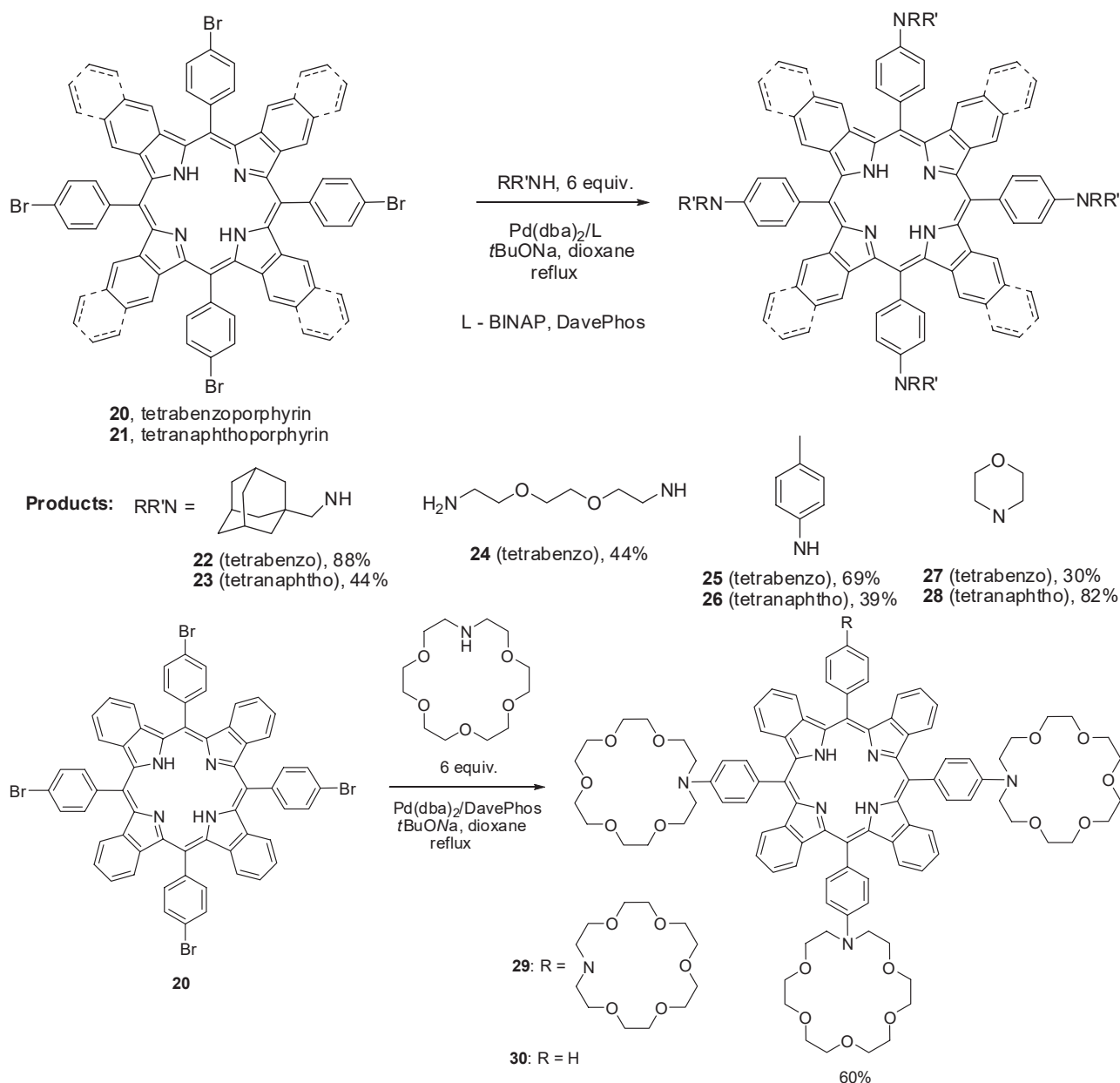
Synthesis of azacrown-porphyrin conjugates with diamine linkers can be achieved by reacting diamino derivative of azacrown ethers with mono- and di-*meso*-(bromophenyl)porphyrins in the presence of the palladium catalyst. Compounds **44** and **45** were obtained also using Pd(0) or Cu(I)-catalyzed amination reactions.<sup>[50]</sup> We have found out that mono(bromophenyl)porphyrin must be employed only as its Zn(II) complex **46** while di(bromophenyl)porphyrin can be introduced in the coupling equally as its Zn(II) complex **13** and free base **37** (Scheme 6). Corresponding bis- and trismacrocycles **47-49** were isolated in 15-20 % yields.<sup>[51]</sup> It was also shown that alternative synthesis using diamino derivatives of porphyrin and bromobenzyl substituted azacrown ethers led exclusively to the catalytic reduction of C-Br bond and no conjugates could be obtained. UV-vis and fluorescence spectra of conjugates **47-49** were studied in the presence of 18 metal cations including alkali and alkali earth metals, widely spread transition metals and heavy metals known to be most important pollutants of water. Trismacrocycle **48** was found to be a sensitive fluorescent chemosensor for Cu(II) cations by full emission quenching,

and the presence of other metals tested did not interfere the detection of copper.

### Synthesis of Porphyrin Dyads and Triads Using Pd(0)-Catalyzed Amination

Our own contribution to the field of catalytic transformation of porphyrins deals mainly with the synthesis of polymacrocyclic compounds comprising one or several porphyrin structural units, the latter are known as porphyrin dyads and triads in which porphyrin macrocycles are combined *via* various linkers. We have shown above that starting from Zn(II) *meso*-(4-bromophenyl)porphyrinate **5** we obtained a series of diamino derivatives (see Scheme 2). Some of them, namely porphyrins **7-9** and **11** were introduced in the catalytic arylation using either the same Zn(II) porphyrinate **5** or analogous Sn(IV) and Ni(II) porphyrinates **50** and **51** (Scheme 7), as a result novel heterometallic porphyrin dyads **52-55** and biszinc porphyrin dyad **56**





Scheme 4.

were synthesized in yields 22–56%.<sup>[52]</sup>  $Pd(dba)_2$ /BINAP catalytic system was used for the synthesis of the majority of compounds while  $Pd(dba)_2$ /DavePhos was employed in the synthesis of tris macrocycles with diazacrown ether linker. Coordination properties of the tweezer **52** with Cu(II) cations and supramolecular organization of tris macrocycle **55** using DABCO were studied.

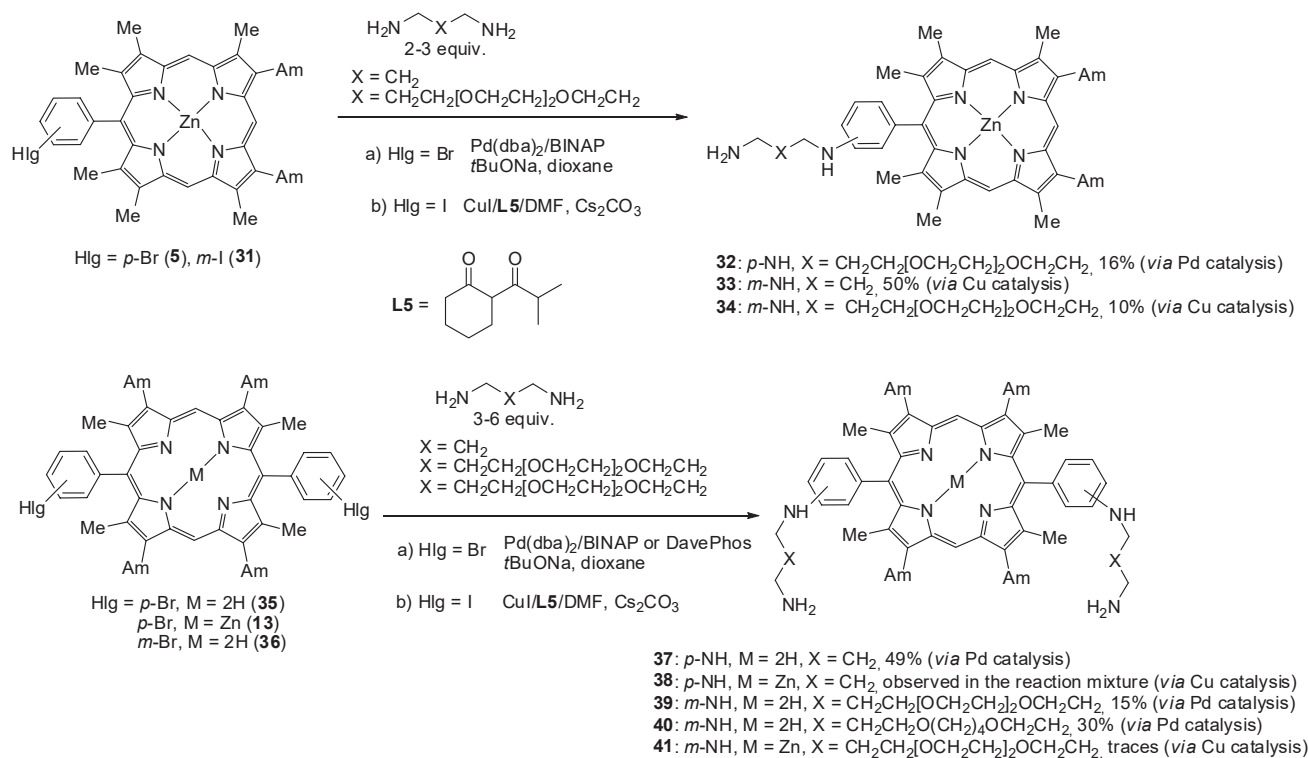
Another approach to bisporphyrin compounds utilizes the possibility of the catalytic *N,N*-diarylation of the primary amino group. Using this approach, diamino derivative **6** was introduced in the reaction with Sn(IV) porphyrinate **50** in the presence of  $Pd(dba)_2$ /DavePhos catalytic system, and the target porphyrin dyad **57** was isolated in 18% yield (Scheme 7). This compound is notable for its diphenylamino linker between two porphyrin units.

Above-mentioned successful synthesis of 5,15-bis-(diamino) derivatives of porphyrins (see Scheme 3) opens a way for more complex compounds, *i.e.* porphyrin triads with diamino linkers. Bis(piperazine) derivative **16** was

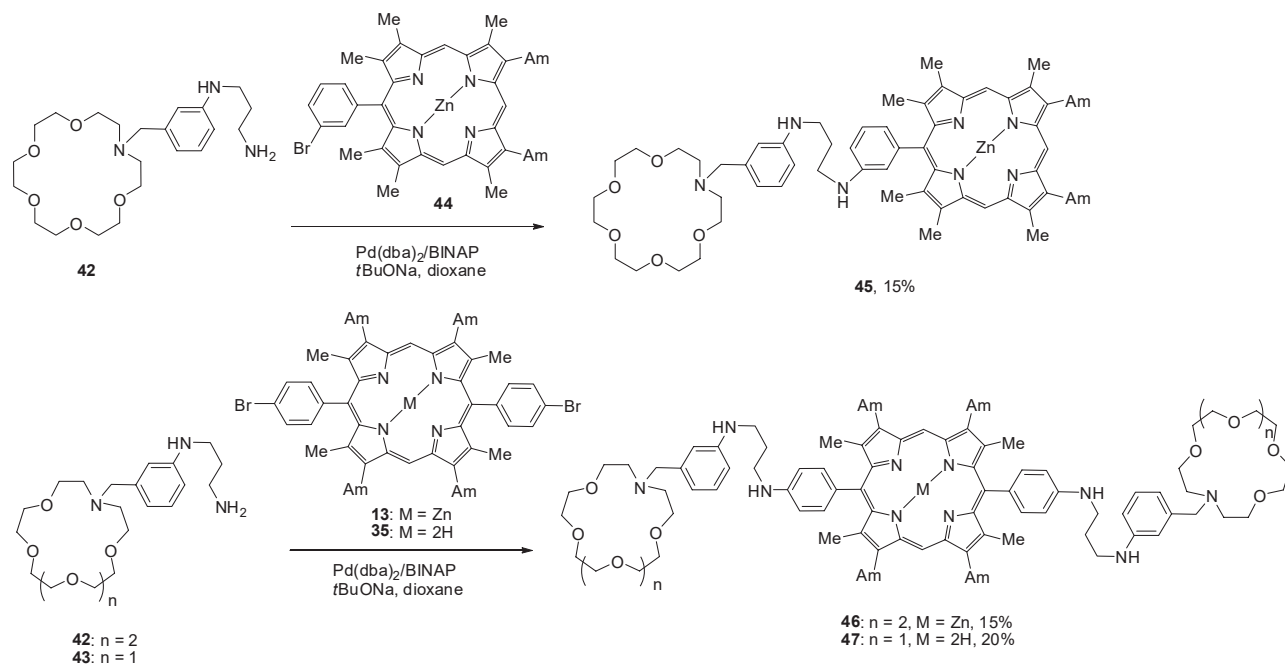
introduced in the reaction with zinc porphyrinate **5** catalyzed by  $Pd(dba)_2$ /DavePhos and the desired triad **58** was obtained in an excellent 75% yield (Scheme 8).<sup>[53]</sup> We verified the importance of the use of Zn(II) complex: the same reaction with a free porphyrin base afforded only 6% yield of the corresponding triad. Pentamacrocyclic porphyrin triad **59** utilizing diazacrown ethers as linkers was obtained *via* a similar reaction employing bis(azacrown) derivative **20** (Scheme 8). It is to be noted that previously, in the course of the synthesis of bis(diamino) derivatives of porphyrins, we noted the formation of porphyrin dyads as by-products when the excess of diamines was insufficient to prevent their *N,N*-diarylation.

The synthesis of the porphyrin triad with a diphenylamino linker can be accomplished using the reaction of 2 equiv. of Zn(II) porphyrinate **5** with another compound, 5,15-di(4-aminophenyl) substituted porphyrin **60** (Scheme 9).<sup>[53]</sup> Corresponding triad **61** was obtained in 21% yield and added to a list of polyporphyrin compounds synthesized *via* Buchwald-Hartwig amination reactions.

## Transition Metal Catalysis in Porphyrin Modifications



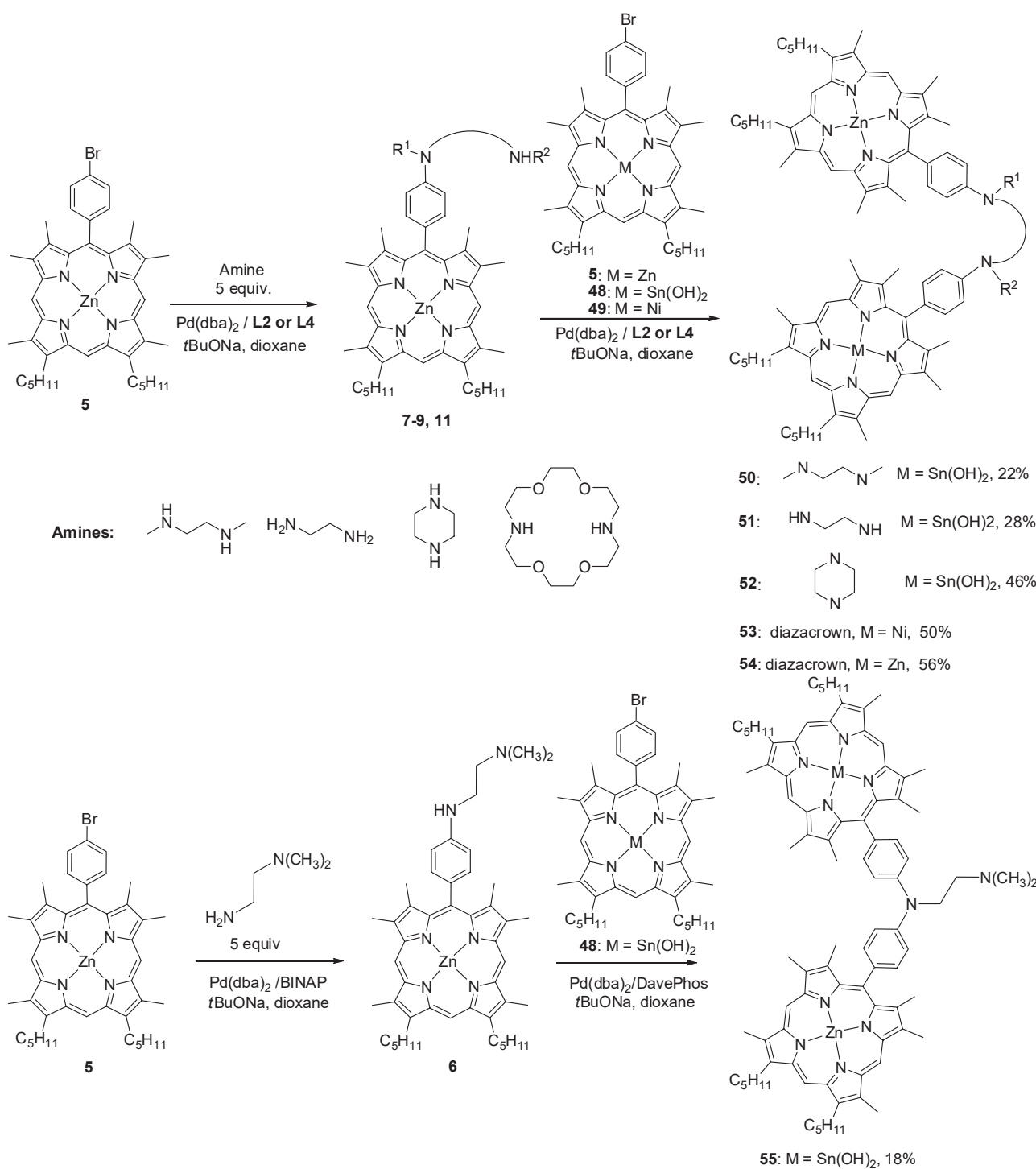
Scheme 5.



Scheme 6.

Cu(I)-catalyzed 1,3-dipolar cycloaddition reactions were successfully used for the synthesis of porphyrin triads containing 1,2,3-triazole linkers. For this purpose two combinations of starting compounds were tried. The first reaction scheme employed 5,15-bis(ethynylphenyl) derivative of porphyrin **62** with 2 equiv. of *meso*-(4-azidophenyl) substituted porphyrin **63** (Scheme 10). Reaction conditions

were adjusted to provide the best yield of the target triporphyrin compound **64**, the best were found to be CuI/DIPEA in THF-MeCN solution which gave 68 % yield of this triad, and a classical system (CuSO<sub>4</sub>/sodium ascorbate in DMF) to provide slightly lower yield 60%.<sup>[54]</sup> According to the second reaction route, 5,15-bis(4-azidophenyl) substituted porphyrin **65** was coupled with 2 equiv. of *meso*-(4-ethynyl-



Scheme 7.

phenyl)porphyrin **66** in the presence of CuI/DIPEA in THF-MeCN (Scheme 11) and it produced an isomeric porphyrin triad **67** in a high 70 % yield. It was also shown that a simpler porphyrin dyad could be easily synthesized by reacting porphyrins **63** and **66** under the same conditions.

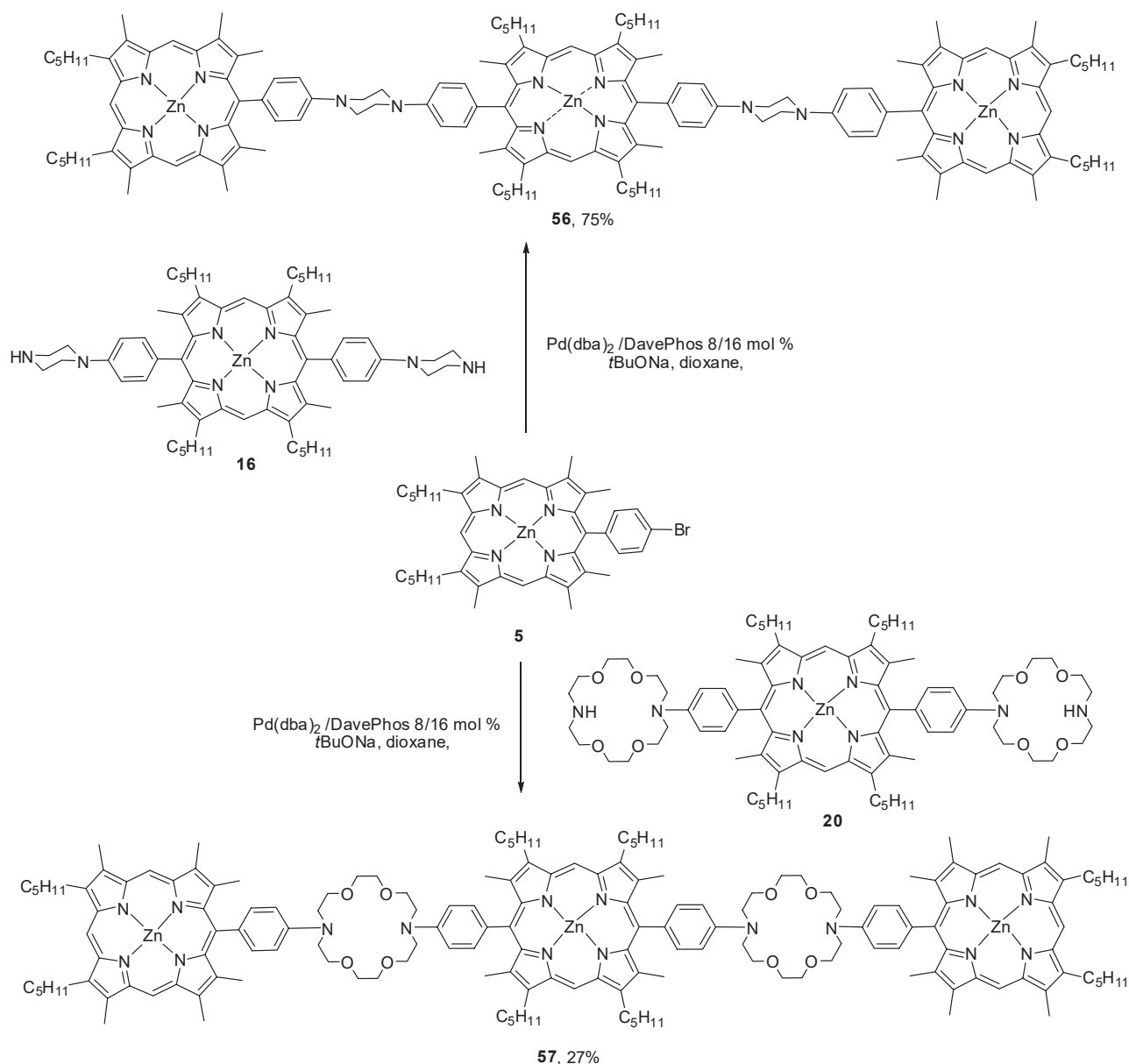
Porphyrin triad of a star shape was successfully synthesized using the similar approach: 1,3,5-tri(ethynyl)benzene was reacted with 3 equiv. of *meso*-(4-azidophenyl)substituted porphyrin **63** and the target triad **68** was isolated in 30 % yield (Scheme 12).<sup>[55]</sup> It is to be mentioned that only zinc porphyrinates but not free porphyrin bases can

participate in these reactions as the latter easily coordinate copper eliminating it from the catalytic cycle.

### Catalytic Modification of Macrocyclic Compounds with Porphyrin Units

Porphyrin moiety possesses valuable optical properties as a strong chromophore and fluorophore group. Thus it was interesting to modify some macrocycles and macrobicycles by porphyrin units for their further examination



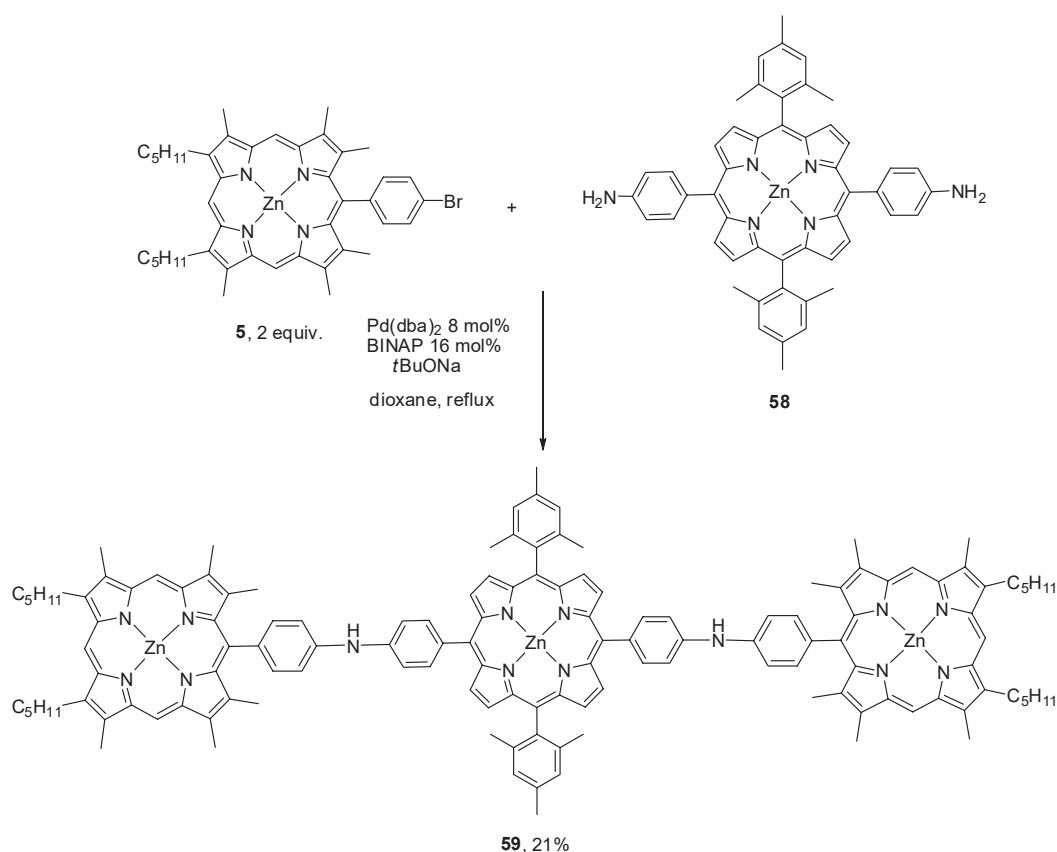


Scheme 8.

as colorimetric and fluorimetric chemosensors for metal cations. Diazatrioxamacrocycle **69** based on 3,3'-disubstituted biphenyl was synthesized according to a previously described method by Pd(0)-catalyzed macrocyclization reaction of 3,3'-dibromobiphenyl with trioxadiazine,<sup>[56]</sup> and macrocycle **70** comprising 2,7-disubstituted naphthalene fragment was obtained by the catalytic amination of 2,7-dibromonaphthalene.<sup>[57]</sup> These macrocycles were introduced in the palladium-catalyzed arylation with 2 equiv. of Zn(II) porphyrinate **5** in the presence of Pd(dba)<sub>2</sub>/DavePhos catalytic system, and the target bisporphyrin derivatives **71** and **72** were isolated in 27 and 18 % yields, respectively (Scheme 13). Our investigations of UV-vis and fluorescence spectra of these compounds in the presence of 18 metal cations revealed that compound **71** could be used as fluorimetric molecular probe for Al(III) and Cu(II) cations as these metals totally quenched the emission, while tris-macrocycle **72** would serve as a perspective fluorimetric chemosensor

for Cu(II) cations as this metal selectively quenched emission and other cations did not interfere.

Macrocycles **73-75** which differ by the size of the central diazacrown ether moiety, nature of the trioxadiazine chain and substitution pattern in aminobenzyl spacers were synthesized *via* Pd(0)-catalyzed macrocyclization reactions using known procedures,<sup>[58]</sup> and they were introduced in the catalytic diarylation reactions with 2 equiv. of Zn(II) porphyrinate **5** (Scheme 14). The yields of the target tetramacrocyclic compounds **76-78** with two porphyrin units ranged from 11 to 23 % and substantial steric hindrances in the macrocycles made this reaction enough difficult. Only Pd(dba)<sub>2</sub>/DavePhos catalytic system was active in this case. These compounds were also tested as possible optical detectors of metal cations and tetramacrocyclic **77** proved to be a perspective fluorescent chemosensor for Cu(II) cations as this metal selectively and fully quenched the emission without interference of other cations.



Scheme 9.

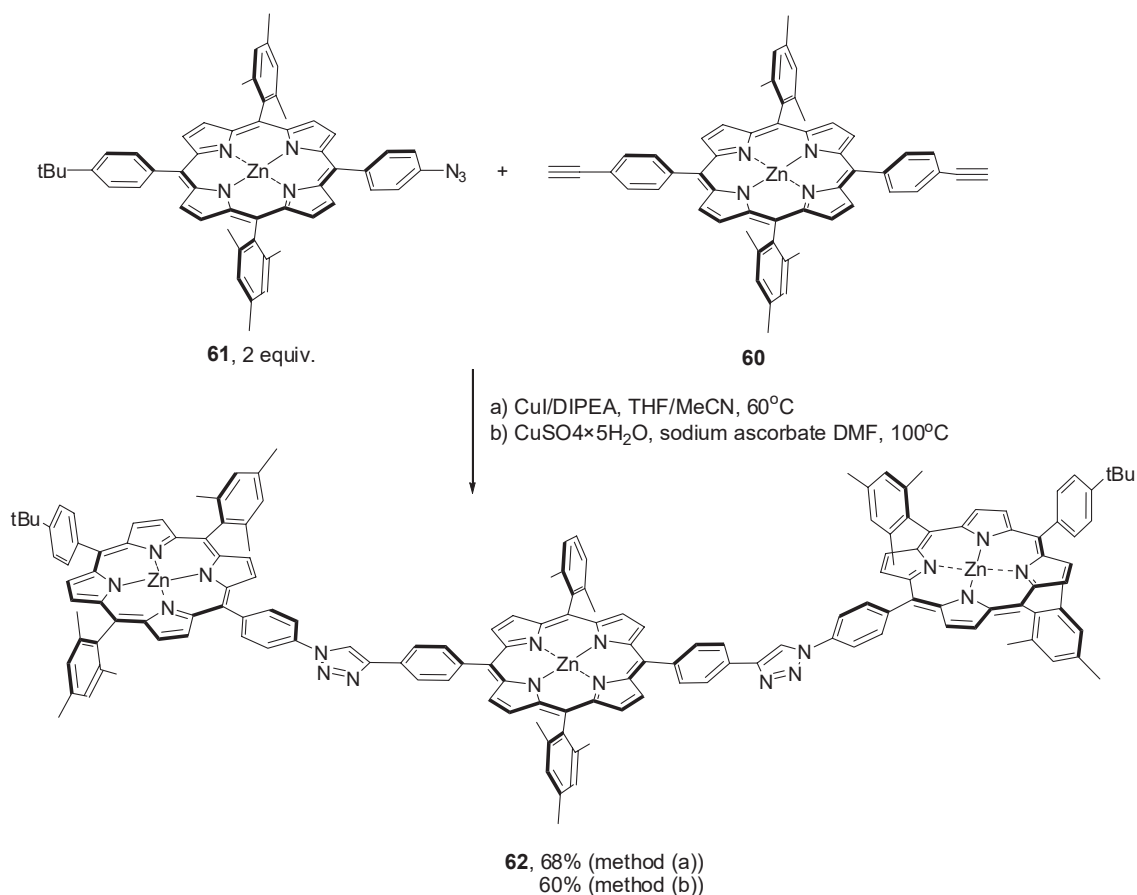
## Conclusions

We demonstrated the possibilities to use palladium and copper-catalyzed amination of halogenophenyl porphyrins for the synthesis of different derivatives of monoporphyrin compounds, including the synthesis of the products of mono-, di-, and tetraamination. This approach was used for the introduction of aza- and diazacrown ethers in the porphyrin core thus giving rise to polymacrocyclic compounds. Pd(0)-Catalyzed amination reactions were successfully employed for the synthesis of porphyrin dyads and triads, as were also Cu-catalyzed 1,3-dipolar cycloaddition reactions which opened a way to porphyrin triads of various architectures. Pd(0)-Catalyzed amination of bromophenyl substituted zinc porphyrinate with nitrogen- and oxygen-containing macrocycles and macrobicycles afforded tris- and tetramacrocyclic compounds which were found useful for creating fluorescent chemosensors for metal cations.

**Acknowledgements.** This work was financially supported by the RSF grant 14-23-00186.

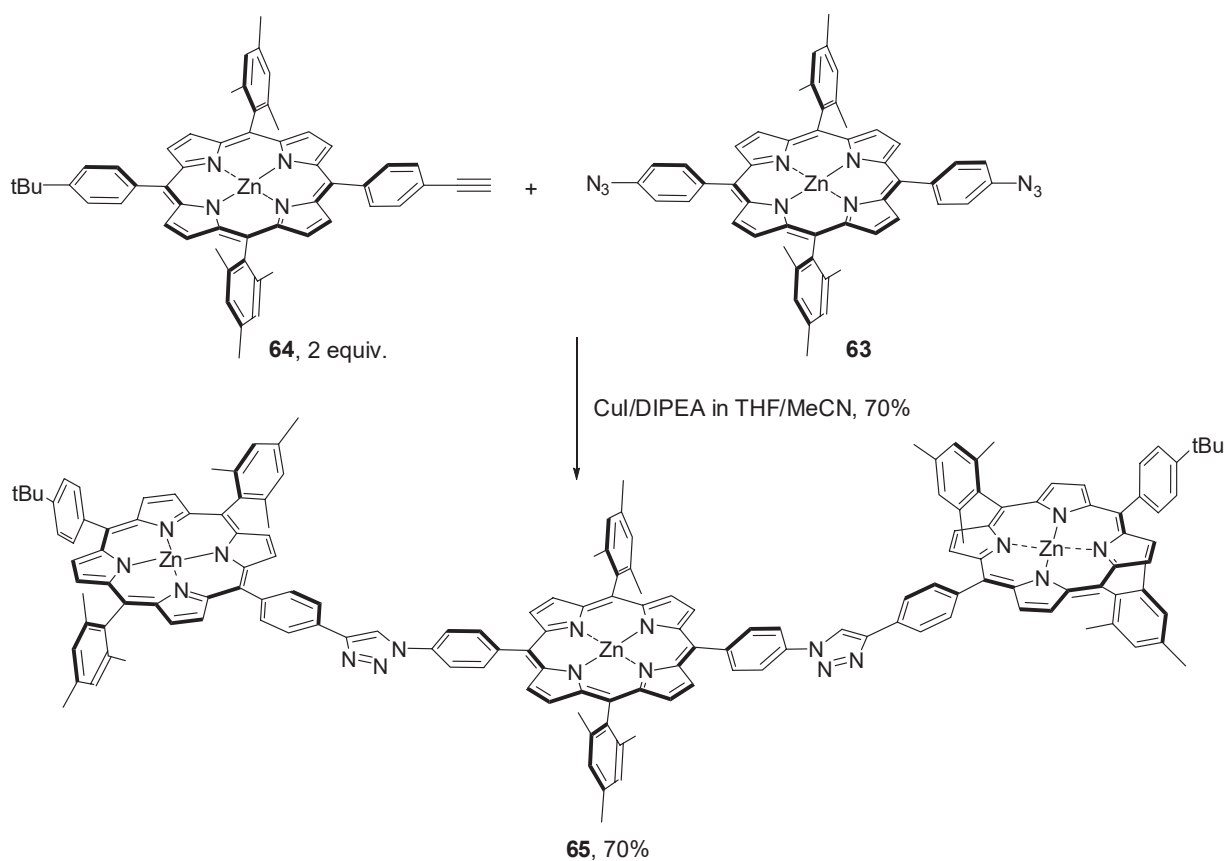
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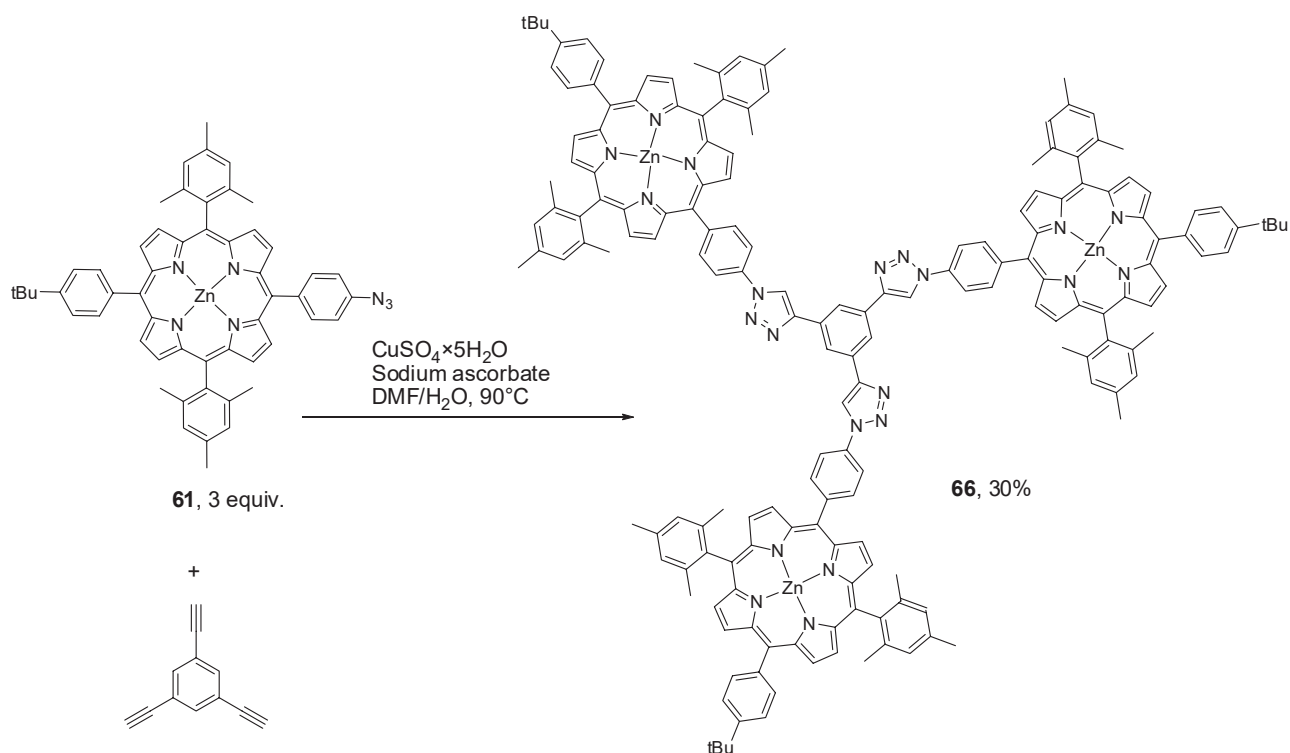


Scheme 10.

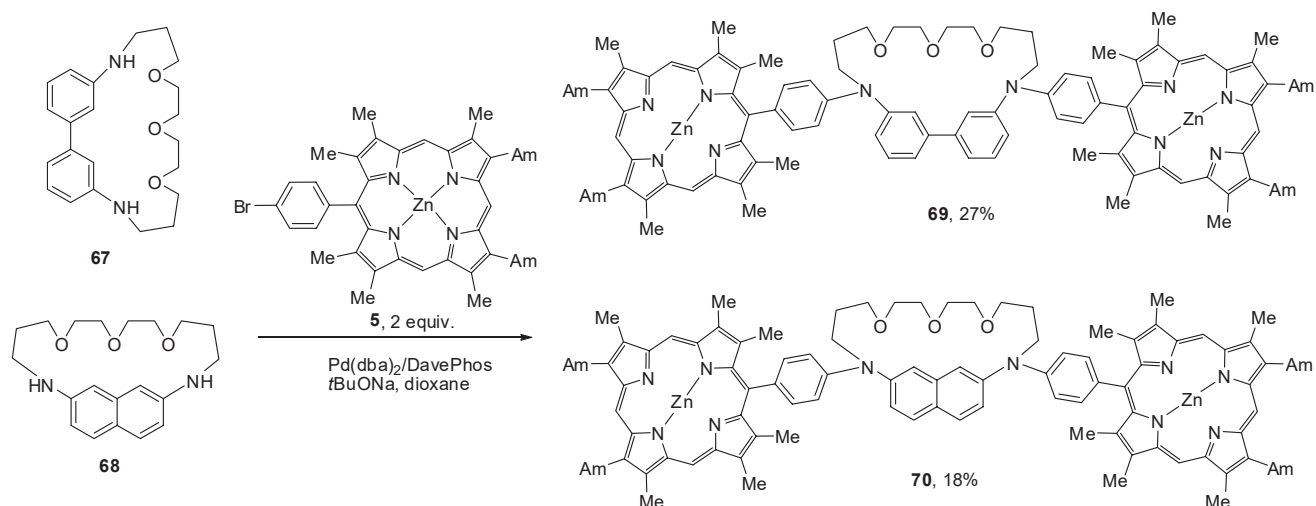
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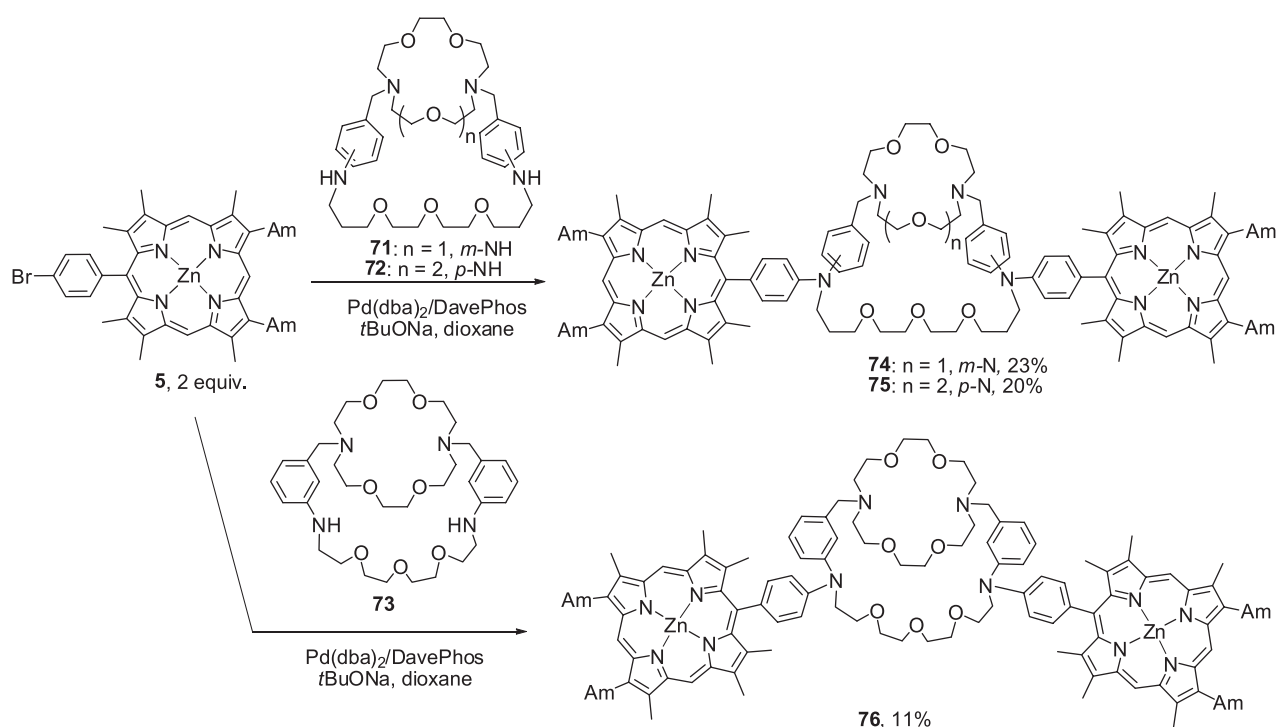
Scheme 11.



Scheme 12.



Scheme 13.



Scheme 14.

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Received 13.05.2016

Accepted 25.05.2016